Preparation of π-Conjugated Poly(hydroquinone-2,5-diyl) and Poly(p-benzoquinone-2,5-diyl) and Their Electrochemical Behavior

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π-Conjugated polymers constituted of redox active units are the subject of many recent papers.[1] Quinones and hydroquinones belong to typical redox active compounds, and their chemical interconversion as well as quinone- or hydroquinone-modified redox active electrodes[2] has extensively been studied. However, examples of well-characterized main-chain type polyquinones and investigation of their electrochemical behavior have been limited.[3]

p-Benzoquinone and hydroquinone are the most simple redox active units, and revealing chemical properties of the polymers containing these units in their main chain is considered to be interesting. Dordick and co-workers[3a] reported preparation of meta-bonded polyhydroquinone by a biochemical process and its interesting electrochemical response. Yamamoto and co-workers[4] reported preparation of a smooth film of poly(dihydroxyphenylene) (or poly(hydroquinone)) by electrooxidative polymerization of hydroquinone. However, in this case, the bonding mode between the monomeric unit in the polymer is controversial (e.g., the polymer may contain a 1,2-bonding unit[4]), and preparation of soluble poly(hydroquinone) by the electrochemical polymerization has not been reported. On the other hand, recently developed organometallic polycondensation[5–7] of dihaloaromatic compounds X–Ar–X give π-conjugated polymers including poly(anthraquinone)s[3b] with well-characterized bonding.

Application of this polycondensation to 2,5-diacetoxy-p-phenylenes gives the corresponding polymers, and chemical transformation of the polymers affords polymers containing the hydroquinone and p-benzoquinone units in their main chain. Herein we report preparation and properties of the polymer containing the 2,5-diacetoxy-p-phenylene, hydroquinone, and p-benzoquinone units.

The following dehalogenative organometallic polycondensation using a zerovalent nickel complex Ni^0L_m[1a,3b] gave poly(2,5-diacetoxybenzene-1,4-diyl)[5] in 86% yield,
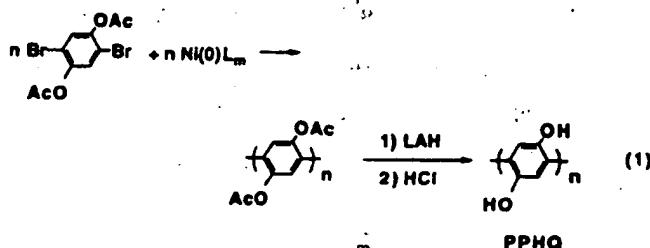
and treatment of the polymer with lithium aluminum hydride afforded poly(p-hydroquinone) (PPHQ)[6] with M_w 8500 (determined by a light-scattering method) and an

$[\eta]$ value of 0.13 dL g^{-1} in DMF. The IR spectrum of PPHQ was almost identical to that of the electrochemically deposited poly(dihydroxyphenylene) film,[4] revealing that the electrochemical oxidative polymerization of hydroquinone proceeded mostly at the 2,5-positions.

PPHQ was soluble in DMF (about 20 mg/mL) and partly (about 70 wt %) soluble in DMSO; however, it was insoluble in CH$_3$CN, CHCl$_3$, toluene, THF, methanol, and H$_2$O. The solubility of PPHQ was better than that of poly(anthraquinone)s without substituents.[3b] In DMF, the π-π* absorption peak (λ_{max} = 298 nm) of hydroquinone was shifted to a longer wavelength (λ_{max} = 345 nm) for PPHQ due to expansion of the π-conjugation system, and the polymer showed a photoluminescence peak at 427 nm in DMF. The absorption peak appeared at a longer wavelength than those of tetra-(hydroquinone) derivatives.[2c]

Figure 1a exhibits a CV chart of a DMF solution of PPHQ under N$_2$. The CV chart shows two oxidation peaks at E_1 and E_2 and two reduction peaks at E_3 and E_4. The CV data are accounted for by the following electrochemical reactions including H$^+$ transfer, which are based on previous reports on the electrochemical behavior of hydroquinone.[7]
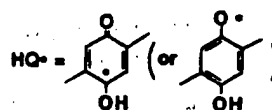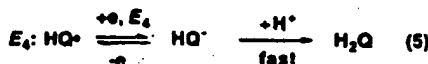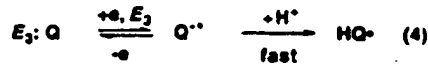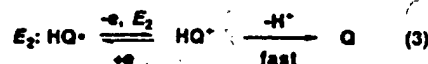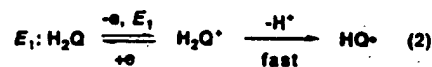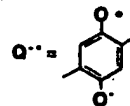
The CV data of PPHQ, however, show some differences from those of hydroquinone. For example, the E_1 and E_2 peaks are more clearly separated in the case of PPHQ.

Repeated scanning gave almost the same CV curve (e.g., in the fifth scanning), suggesting that the polymer was stable in the solution. The peak electric current is proportional to $v^{1/2}$ (v = sweeping velocity) in a v range of 50–900 mV s^{-1}. Use of [NBu$_4$]BF$_4$ as the electrolyte also gave analogous CV data, although an additional n-undoping peak (vide infra) at about −0.8 V vs Ag/Ag$^+$ was observed. Chemical oxidation of PPHQ with NO$_2$ gave a black solid whose IR spectrum showed a ν(C=O) peak characteristic of quinone at 1654 cm^{-1}.

In contrast to the solution system, the CV curve of a PPHQ film[8] in a CH$_3$CN solution strongly depended on
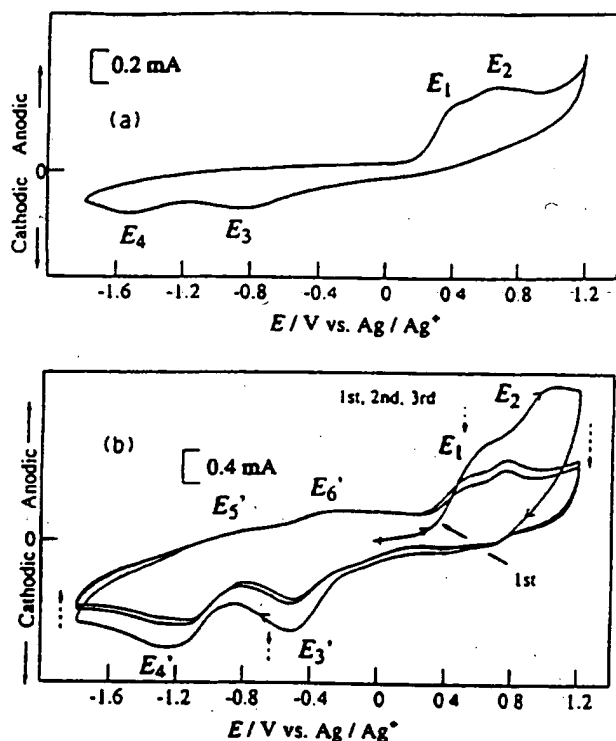
Figure 1. Cyclic voltammograms of (a) PPHQ (1 mM) in a DMF solution containing 0.1 M of [NEt₄]ClO₄ (sweeping velocity = 200 mV s⁻¹) and (b) a film of PPHQ cast on a Pt plate immersed in a CH₃CN solution containing 0.1 M [NBu₄]-PF₆ (sweeping velocity = 20 mV s⁻¹). A Pt plate (1 cm × 1 cm) is used for both.

the repeating number of scanning. As shown in Figure 1b, the large oxidation peaks at E_1 and E_2, which are observed at the first scanning and correspond to the oxidation of PPHQ to PPQ, become very small in the second scanning. The CV data observed at the second and after the second scanning are explained by n-doping of poly(*p*-quinone) (PPQ), which is formed by oxidation of PPHQ in the first CV cycle.

When a sufficiently thin film was used at relatively slow sweeping velocity v, the anode peak current observed at E_2 in the first scanning was roughly proportional to v,[9] revealing that the mass of the polymer controlled the anodic current (eq 6). The anodic current
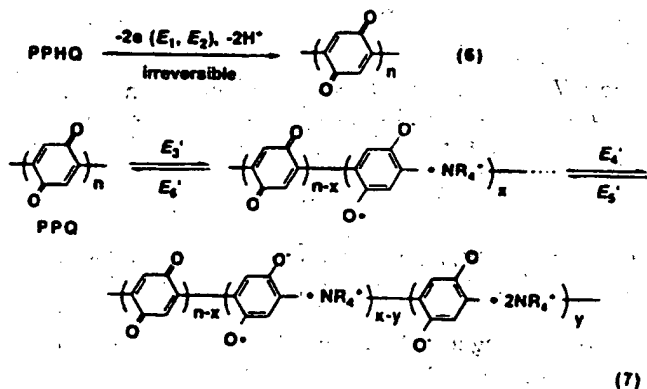
observed with the thin film corresponds to oxidation of about 85–95% of the hydroquinone unit to the quinone unit.

The rapid decrease in the anodic current in the second scanning for the film of PPHQ is reasonably accounted for by assuming that the film releases H⁺ generated in the oxidation processes (eqs 2 and 3) to the solution

whereas the Q species in the film cannot capture H⁺ from the solution smoothly during its reduction processes. If the quinone unit Q in the film cannot capture H⁺, the hydroquinone species H_2Q is not regenerated, and the $Q^{\cdot-}$ and Q^{2-} species formed during the reduction processes will capture NR_4^+ instead of H⁺ to give the n-doped state (eq 7). Thus, the cathodic reactions with peaks at E_3' and E_4' (Figure 1b) are explained by the n-doping of poly(*p*-quinone) (PPQ), and the E_5' and E_6' peaks are assigned to n-undoping peaks as shown in eq 7.

Although similar electrochemical n-doping reactions have been proposed for π-conjugated poly(anthraquinone-1,5-diyl)s,[3b] this is the first example of n-doping of the simplest π-conjugated polyquinone. In the case of poly-(anthraquinone-1,5-diyl)s, the quinone unit is not included in the π-conjugated poly(*p*-phenylene) main chain, and the present results give more direct information about the redox behavior of the quinone unit in the π-conjugated main chain. The anion or negative carrier in the polymer is considered to be delocalized along the π-conjugated system. Essentially the same CV data were obtained with various electrolytes ([NEt₄]BF₄, [NBu₄]ClO₄, and [NBu₄]BF₆).[10]

The above data indicate that the electrochemical behavior of PPHQ strongly depends on whether the polymer is in solution or in the solid state (film); the film may provide hydrophobic circumstances for the quinone unit. CV analysis of the polymer film in aqueous media gave analogous results, suggesting that the irreversible oxidation of PPHQ to PPQ also took place even in the aqueous media. The position of the E_1 peak received minor effects from the pH value of the solution. On the other hand, the E_2 peak was shifted to a higher potential with an increase in the acidity of the aqueous solution. At pH values of 1.0, 2.0, 4.0, 6.0, and 7.0, respective E_2 values of 1.24, 1.23, 1.10, 1.05, and 0.88 V vs Ag/Ag⁺ were obtained.

References and Notes

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(5) IR (KBr, cm⁻¹): 2932, 1762 (vs), 1207 (vs). ¹H NMR (DMF-d_7): (ppm): 7.6–6.9 (m, 2H), 2.6–2.0 (m, 6H); the peaks are split probably due to the presence of conformers. Elemental analysis roughly agreed: Found: C, 61.5; H, 4.5. Calcd: C, 62.5; H, 4.2.

(6) Yi ld = 100%. IR (KBr, cm⁻¹): 3390 (vs), 1605 (s), 1400 (vs), 1190 (vs). ν(C—O) f the OAc is not observable. Analytical

data agree with a hydrated structure: Found: C, 57.2; H, 5.2. Calcd for $(C_6H_4O_2 \cdot H_2O)_n$: C, 57.1; H, 4.8. $[\eta] = 0.13$ dL g^{-1} in DMF at 30 °C. $M_w = 8500$ (light scattering in DMF). $M_n = 3400$ (GPC, DMF, and polystyrene standards).

(7) (a) Paker, V. D. *Electrochim. Acta* **1973**, *18*, 519. (b) Bard, J. A.; Lund, H., Eds. *Encyclopedia of Electrrochemistry of the Elements*; Marcell Dekker: New York; 1978, XI 272 and XII 198. (c) Paker, V. D.; Eberson, L. *J. Chem. Soc, Chem. Commun.* **1970**, 1289. (d) H_2Q in DMF (0.1 M [NEt$_4$]BF$_4$) gives the CV peaks (at 0.41 V (E_1), 0.85 V (E_2), −0.77 (E_3), and −1.34 V (E_4) at almost the same position as H_2Q in CH$_3$CN.[7a-c]

(8) Cast from a DMF solution (9.3 mM monomer unit) of PPHQ on a Pt (1 cm × 1 cm) or ITO electrode and dried under vacuum.

(9) Data obtained with film corresponding to 9.3×10^{-8} mol of monomer unit/cm^2 and in a sweeping velocity (v) range of 30−70 mV s^{-1}. With a thicker film or faster v, the degree of oxidation decreases (e.g., about 50% with a film corresponding to 2.8×10^{-7} mol monomer unit per cm^2 and v of 90 mV s^{-1}).

(10) Use of LiBF$_4$, however, gives quite different results. The E_3' and E_4' n-doping peaks are observed only in the first scanning, and the n-undoping peak (E_5' and E_6') is not observable. Even the E_3' and E_4' peaks disappear in the repeated scanning. Similar results have been reported for π-conjugated poly(anthraquinone)s,[3b] and the results are ascribed to the known high stability of the Li$_2$Q[3b] (dilithium salt of hydroquinone) type product formed in the first scanning and its inertness to the electrochemical oxidation (or n-undoping). The E_5' and E_6' peaks merge in the CH$_3$CN solution of [NBu$_4$]ClO$_4$ to give a peak, and the peak current gradually increases with the scanning time.